RT - from SLP

PROTOCOL FOR THE SAMPLING AND ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS AND PHENOLICS IN WATER

1.0 INTRODUCTION

1.1 Analytical Monitoring Overview

The objectives of this project are to monitor contaminants [polynuclear aromatic hydrocarbons (PAH) and phenolics] in drinking water for the City of St. Louis Park and selected neighboring communities, and to monitor all aquifers (i.e., Drift-Platteville, St. Peter, Prairie du Chien-Jordan, Ironton-Galesville and Mt. Simon-Hinckley) underlaying the old Reilly Tar site in St. Louis Park, Minnesota.

Analysis of these samples will be used to monitor contaminant occurance in drinking water, and for compliance purposes (i.e., exceedence of Drinking Water Criteria and Advisory Levels, Cessation Criteria, and Future Sampling Frequency) specified in the Remedial Action Plan (RAP). This protocol is designed to determine those contaminants associated with the RAP that are amenable to gas chromatography/mass spectrometry analysis. This document provides procedures for trace organic analysis of water samples, documentation of methods and their performance, and verification of the sample data generated.

The Contractor shall furnish the necessary personnel, materials, services and facilities, and otherwise do all things necessary for or incident to laboratory support for field sampling, and capillary GC/MS analysis of samples.

1.2 General Information

This project doesn't represent the usual type of sampling and analysis commonly undertaken for environmental monitoring purposes; it must be carried out with considerable care and with due regard for the purposes and requirements of all monitoring performed.

Since the analytical data generated by this method is interpreted for compliances purposes, the quality control, verification and reliability of the data is important particularly with respect to drinking water supply wells whose water exceeds the Drinking Water Criteria or Advisory Levels. Further, it is important to track the movement of contaminants in all aquifers. It is also important, for Cessation Criteria, and possibly for scheduling future sampling frequencies for various wells, to have the ability to analyze trends in aquifer water quality.

The sampling apparatus for on-site adsorption and concentration of PAH and Phenolics, samples a continuous flowing aquifer water supply. The sampling apparatus is connected to the aquifer water supply by an all Teflon manifold. The Teflon manifold is designed to collect samples in duplicate by splitting the flow with a tee. A constant flow of water passes through two SEP-PAK pairs (C_{18} filled, small capacity resin cartridges manufactured by Waters Corporation), one pair on each side of the tee, removing particulate and soluble organics from the water. At the end of the sampling period, the water volume sampled is measured by weight. Following the sampling, the SEP-PAK pairs are solvent extracted.

The prepared extracts are analyzed for the list of PAH and Phenolics in Table 4.1, and isotopically-labeled field and laboratory standards in Table 4.2 using capillary gas chromatography/mass spectrometry (GC/MS). The analyst must optimize the GC/MS system conditions to achieve maximum sensitivity so that the system is capable of detecting 1ng of benzo(a)pyrene or dibenz(a,b)anthracene on column, and 2ng of carcinogenic and other PAH and Phenolics on column.

This document is not intended to be an exhaustive, definitive protocol for communicating all absolute procedures for conducting this project. However, it is expected that this protocol will be executed by experienced and qualified persons.

1.3 Sampling Schedule

A sampling schedule for the first and second monitoring years following the effective date is provided in Tables 1.1, 1.2, 1.3, 1.4, 1.5 and 1.6. The sampling schedule tables are organized by years and by the well's functional purpose into the following tables.

- Municipal Drinking Water - Tables 1.1 and 1.2 include municipal drinking water wells for St. Louis Park and surrounding communities and contaminated wells (SLP 10 & 15) operated with GAC treatment to achieve levels which meet the Drinking Water Criteria for St. Louis Park's potable water distribution system. These tables also include samples for the feed water samples to the GAC system and the wellhead water from SLP 10 & 15.

- Gradient Control Wells - Tables 1.3 and 1.4 include wells which are pumping untreated discharge water to the sanitary sewer or surface waters. The purpose of these wells is to prevent the spread of ground water exceeding the Drinking Water Criteria. It should be noted that the monitoring frequency will be regulated by NPDES and MWCC permits and, therefore, more frequent sampling may be required.

- Source Control and Monitoring Wells - Tables 1.5 and 1.6 include source control wells located on the old Reilly Tar site and wells used to determine the nature and extent of the contamination in the St. Peter aquifer.

Each sampling schedule table further breaks down the wells by aquifer (e.g., St. Peter, Prairie du Chien-Jordan, etc.). These tables do not identify specific wells which will be analyzed in duplicate for quality control purposes. However, the field sampling system is designed to collect samples simultaneously in duplicate for QA/QC purposes.

The table sample volume column specifies the volume of water to be sampled (i.e., passed through the macroreticular resin cartridges) at each well. The volume indicated in the column is based upon a maximum amount which can be safely passed through the resin cartridges before component breakthrough (i.e., 45 liters) and/or the concentration of pollutants in the water supply. Ideally, the total amount of pollutants absorbed onto the resin cartridges should be approximately equal from well to well, and is controlled by the volume of water passed through the

resin cartridges. On new well installations, the volume will be based upon pollutant concentrations in surrounding wells. Well volumes may be adjusted accordingly on subsequent monitorings to maximize the analytical information, reliability and precision and accuracy.

TABLE 1.1: Sampling Schedule for Municipal Drinking Water Wells

SAMPLE IDENTIFICATION	MONTHLY SAMPLING SCHEDULE												SAMPLE VOLUME (Liters)
	1	2	3	4	5	6	7	8	9	10	11	12	
GAC TREATED MUNICIPAL DRINKING WATER													
Prairie duChien-Jordan Aquifer													
SLP10	8	3	1	1	1	1+	1	1	1	1	1	1	45
SLP15	8	3	1	1	1	1+	1	1	1	1	1	1	45
SLP10/15 (Feed Water)	10	2		2			2			2			10
GRADIENT MUNICIPAL/CONTROL DRINKING WATER													
Mt. Simon-Hinckley Aquifer													
SLP11						1							45
SLP 12						1							45
SLP 13						1							45
SLP 17						1							45
Prairie duChien-Jordan Aquifer													
SLP 6		1			1			1			1		45
SLP 7 or 9		1			1			1			1		45
SLP 14						1						1	45
SLP 16						1						1	45
Edina Municipal Well 2						1						1	45
Edina Municipal Well 3								1					45
Edina Municipal Well 13						1						1	45
Edina Municipal Well 15								1					45
Hopkins Municipal Well 3						1						1	45
Hopkins Municipal Well 6								1					45
Minnetonka Municipal Well 6								1					45
SLP 10 or 15 (Wellhead Water)						1						1	10

LEGEND: (+) Extended Analysis - All compounds listed in Table 4.1 and any other compounds which are detected with peak heights $\geq$ 5 X signal to noise shall be identified and, if possible, quantified, using a mass spectral library.

TABLE 1.2: Sampling Schedule for Municipal Drinking Water Wells

SAMPLE IDENTIFICATION	MONTHLY SAMPLING SCHEDULE												SAMPLE VOLUME (Liters)
	13	14	15	16	17	18	19	20	21	22	23	24	
GAC TREATED MUNICIPAL DRINKING WATER													
Prairie du Chien-Jordan Aquifer													
SLP10	1			1			1+			1			45
SLP15	1			1			1+			1			45
SLP 10/15 (Feed Water)							2						10
GRADIENT MUNICIPAL/CONTROL DRINKING WATER													
Mt. Simon-Hinckley Aquifer													
SLP11						1							45
SLP 12						1							45
SLP 13						1							45
SLP 17						1							45
Prairie duChien-Jordan Aquifer													
SLP 6		1			1			1			1		45
SLP 7 or 9		1			1			1			1		45
SLP 14						1						1	45
SLP 16						1						1	45
Edina Municipal Well 2						1						1	45
Edina Municipal Well 3								1					45
Edina Municipal Well 13						1						1	45
Edina Municipal Well 15								1					45
Hopkins Municipal Well 3						1						1	45
Hopkins Municipal Well 6								1					45
Minnetonka Municipal Well 6								1					45
SLP 10 or 15 (Wellhead Water)						1						1	10

LEGEND: (+) Extended Analysis - All compounds listed in Table 4.1 and any other compounds which are detected with peak heights _ 5 X signal to noise shall be identified and, if possible, quantified, using a mass spectral library.

TABLE 1.3: Sampling Schedule for Gradient Control Wells

SAMPLE IDENTIFICATION	MONTHLY SAMPLING SCHEDULE												SAMPLE VOLUME (Liters)
	1	2	3	4	5	6	7	8	9	10	11	12	
GRADIENT CONTROL MONITORING WELLS													
Prairie duChien-Jordan Aquifer													
SLP 4+		1			1			1			1		40
W 29								1					10
W 40								1					45
W 48		1			1			1			1		20
W 70								1					20
W 119						1						1	45
W 401								1					▲
W 402						1						1	▲
W 403						1						1	▲
American Hdwr. Mutual						1						1	45
Drift-Platteville Aquifers													
Well # Not Available		1			1			1			1		∞

LEGEND: (+) Discharge to surface water, Nation Pollution Discharge Elimination System permit.
(▲) Sample volume to be determined based on well location.

TABLE 1.4: Sampling Schedule for Gradient Control Wells

SAMPLE IDENTIFICATION	MONTHLY SAMPLING SCHEDULE												SAMPLE VOLUME (Liters)
	13	14	15	16	17	18	19	20	21	22	23	24	
GRADIENT CONTROL MONITORING WELLS													
Prairie duChien-Jordan Aquifer													
SLP 4+						1						1	40
W 29								1					10
W 40								1					45
W 48		1			1			1			1		20
W 70								1					20
W 119						1						1	45
W 401								1					▲
W 402						1						1	▲
W 403						1						1	▲
American Hdwr. Mutual						1						1	45
Drift-Platteville Aquifers													
Well # Not Available		1			1			1			1		

LEGEND: (+) Discharge to surface water, National Pollution Discharge Elimination permit.
(▲) Sample volume to be determined based on well location.

TABLE 1.5: Sampling Schedule for Source Control and Monitoring Wells

SAMPLE IDENTIFICATION	MONTHLY SAMPLING SCHEDULE												SAMPLE VOLUME (Liters)
	1	2	3	4	5	6	7	8	9	10	11	12	
SOURCE CONTROL MONITORING WELLS													
Ironton-Galesville Aquifer													
W 105+		1			1			1			1		1
Prairie duChien-Jordan Aquifer													
W 23+		1			1			1			1		1
Drift Aquifer													
Well # Not Available +, *		1			1			1			1		0.5
Platteville Aquifer													
Well # Not Available +, *		1			1			1			1		1
MONITORING WELLS													
St. Peter Aquifer													
SLP 3	1					1						1	45
W 14	1					1						1	1
W 24	1					1						1	2
W 33	1					1						1	2
W 122	1					1						1	10
W 129	1					1						1	10
W 133	1					1						1	45
P 116	1					1						1	45
Five (5) New Wells	5					5						5	▲
Drift-Platteville Aquifers													
W 131	1						1						20
W 136	1						1						20
Six (6) New Wells		6					6						▲
Thirty (30) Existing Wells		30								30			0.5-10, ▲

LEGEND: (+) Discharge to Sanitary Sewer, Metropolitan Waste Control Commission permit.
(*) Each well located within 500 ft. downgradient of monitoring well W13.
(▲) Sample volume to be determined based on well location.

TABLE 1.6: Sampling Schedule for Source Control and Monitoring Wells

SAMPLE IDENTIFICATION	MONTHLY SAMPLING SCHEDULE												SAMPLE VOLUME (Liters)
	13	14	15	16	17	18	19	20	21	22	23	24	
SOURCE CONTROL MONITORING WELLS													
Ironton-Galesville Aquifer													
W 105+				1						1			1
Prairie duChien-Jordan Aquifer													
W 23+				1						1			1
Drift Aquifer													
Well # Not Available				1						1			0.5
Platteville Aquifer													
Well # Not Available				1						1			1
MONITORING WELLS													
St. Peter Aquifer													
SLP 3	1					1						1	45
W 14	1					1						1	1
W 24	1					1						1	2
W 33	1					1						1	2
W 122	1					1						1	10
W 129	1					1						1	10
W 133	1					1						1	45
P 116	1					1						1	45
Five (5) New Wells	5					5						5	▲
Drift-Platteville Aquifers													
W 131													20
W 136													20
Six (6) New Wells		6					6						▲
Thirty (30) Existing Wells		30									30		0.5-10, ▲

LEGEND: (+) Discharge to Sanitary Sewer, Metropolitan Waste Control Commission permit.
(*) Each well located within 500 ft. downgradient of monitoring well W13.
(▲) Sample volume to be determined based on well location.

2.0 REPORTING REQUIREMENTS AND DELIVERABLES

The Contractor shall provide reports and other deliverables specified hereunder. Specific reports are described below.

2.1 Report Description

Following each sampling event, the contractor shall submit a written report within 21 days of sample collection. Each written data report should include:

2.1.1 Sample Tabulation

Tabulation of samples received, date of collection, field log notebook and page #, sample bill of lading (if samples shipped by commercial carrier), date sample received by lab, date sample extracted, date sample analyzed, mass spec log #, DFTPP tune data file # corresponding to sample, GC/MS magnetic tape file #, and description of any problems encountered.

2.1.2 Sample Data Tabulated

Results (identification and quantity) of all PAH and Phenolic individual compounds (see Table 4.1), totals for carcinogenic and other PAH compounds, validated and signed in original signature by the Laboratory Manager.

2.1.3 Analyte Reporting Requirements

Concentrations of PAH and Phenolics less than the lower confidence limit (LCL) of the 95% confidence interval of the calculated MDL are reported as not detectable (ND). Signals present but greater than the LCL of the 95% confidence interval of the calculated MDL and less than

the MDL are reported as less than (<).

2.1.4 GC/MS Tapes

Each GC/MS run on tape should contain the following header information at minimum; identifying run number, sample identification, date and time of sample run, run description (GC column used, temperature program, volume of extract, and injection volume), scan time in seconds, mass range scanned, time of scan (time from start of run) and total intensity of scan (not normalized).

2.1.5 Extended Analysis

During the extended analysis of GAC treated water from SLP 10 and/or 15, any compounds listed in Table 4.1, or any other compounds which are detected with peak heights (5 X signal to noise), shall be identified using a mass spectral library and, if possible, quantitated (if response factor is unknown, estimate concentration by assuming a response factor of 1, and estimate the concentration by comparison of the peak area to the internal standard area).

2.2 QA/QC Report Description

The contractor shall submit a written QA/QC report for each sampling period or group of samples.

2.2.1 Document Control and Chain-of-Custody

All documents including logbook pages, sample tracking records, chromatographic charts, computer printouts (EICP, mass spectra, etc.), raw data summaries, correspondence

and other written documents shall be compiled and maintained by the contractor.

2.2.2 Blank/Duplicate/Spike Data

Data report to include results of isotope spike analyses (% recovery), method blanks, sample duplicates and solvent blank sample analyses (see Appendix 3).

2.2.3 PAH and Phenolics Standards Data

Data report to include listing of samples in a data set for which the standards apply. Correlation coefficient and slope of multi-point standards calibration.

2.3 Contingent Monitoring Due to Exceedence

If the analytical result of any sample taken from an active municipal drinking water well exceeds an advisory level, the results of the reanalysis performed in response to an exceedence shall be within 30 days of taking the sample.

3.0 LABORATORY CAPABILITIES

Each bidder will submit in writing with its bid the Contractor's claim for meeting the requirements provided in sections 3.1, 3.2 and 3.3. This written capabilities document will be used to compare potential Contractors on the basis of personnel, facilities, past experience and quality.

This analytical protocol utilizes a macroreticular resin system for concentrating trace organics and analytical procedures that are significantly different from standardized methodologies (as used for Priority Pollutant analysis, for example). The contractor is asked to state its trace level GC/MS analysis capabilities and specifically those related to PAH analysis.

3.1 Analytical Instrumentation

The Contractor will provide analytical equipment and expertise for this project as specified below:

3.1.1 For use on this contract, the Contractor will, at the Contractor's facility, own or have exclusive in-house use of a gas chromotograph/mass spectrometer/data system that is proven to be fully debugged and operational.

3.1.2 The Contractor's instrument systems will have the following:

(a) The computer will be interfaced by hardware to the mass spectrometer and be capable of acquiring continuous full mass scans for the duration of the chromatographic program as specified in Appendix 2., Section 6.3

(b) The computer will be equipped with mass storage devices for saving all raw data from the GC/MS runs.

(c) Computer software will be available to allow searching GC/MS data for specific ion intensities and plotting these intensities with respect to time or scan number.

(d) The GC/MS will be equipped with a direct on-column capillary injector and/or a split/splitless injector. The fused silica capillary column must be coupled to the mass spectrometer ion source in a way to minimize analyte losses and provide acceptable calibration points at a detection limit specified for each individual compound listed in Table 4.1.a and Table 4.1.b.

(e) The Contractor will have access to a computerized MS library search system capable of providing reverse comparison and forward comparison, and of utilizing the standard spectra contained in the current EPA/NIH Mass Spectral Database.

(i) The system will be able to provide a numerical ranking of the standard spectra most closely corresponding to the unknown spectra examined.

(ii) The data system will provide the processing capability to subtract background spectra from unknown raw spectra, and of significant ions in a spectrum according to the Biller-Biemann algorithm or its performance equivalent.

3.2 Personnel

The Contractor will provide personnel and adequate back-up of key activities and functions as specified below:

3.2.1 The Contractor's GC/MS operators performing work on this project will each have at least 12 months' experience in the operation of the GC/MS/DS on environmental samples.

3.2.2 The GC/MS spectral interpretation specialist performing work on this project will be a Ph.D. level individual with at least one year of experience in the manual interpretation of unknown mass spectra or equivalent.

3.2.3 The Contractor's extraction/fractionation specialist performing work on this project will be a B.S. level individual with at least two years' experience in the preparation of extracts from environmental samples.

3.2.4 The Contractor's standards and sample preparation specialist must have at least six (6) months' experience in the use of a glovebox for the handling of toxic and carcinogenic materials. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the solvents, chemical standards, etc. specified in this method. Exposure to these chemicals must be reduced to the lowest possible level.

4.0 ANALYTICAL PROTOCOL

4.1 General Requirements

The Contractor will use proven instruments and techniques to identify and measure the concentrations unlabelled and isotopically-labelled PAH and Phenolic compounds as listed in Section 4.3.

The Contractor will prepare standards and samples for analysis using preparation procedures in Appendix 1 and extraction procedures in Appendix 2. The Contractor will then subject the extracts to fused silica capillary GC/MS analysis. These extracts will be analyzed to achieve the method detection limits provided in Section 4.3, Table 4.1.

4.2 Specific Requirements

The Contractor will follow the protocols established for sample preparation, analysis, storage and preservation before and after the analysis. The Contractor is advised that the samples may contain levels of potentially toxic organic materials of unknown structure and concentration, and they should be handled throughout the analyses with appropriate caution.

During preparation, the Contractor will spike samples with isotopically labeled standards as listed in Section 4.3, Table 4.2. Isotopically enriched compounds will serve as field standards (i.e., added to the SEP-PAK cartridges prior to field sampling to monitor field sampling recovery) and as laboratory standards (i.e., added to the SEP-PAK cartridges prior to

extraction to monitor laboratory performance). All sample extracts will be spiked with d_{10}-anthracene internal standard before analysis.

In Appendices 1 and 2 the Contractor is provided with the specific analytical procedures to be used, including instructions for sample preparation, sample extraction, mass spectrometric analysis and data interpretation. Specific ions used for searching the mass spectral data are the responsibility of the Contractor. The Contractor is encouraged to use EPA specified ions for quantitation of compounds contained in the priority pollutant list.

The Contractor will perform the following tasks:

4.2.1 Preparation of Field Sampling Equipment

a. Supply and clean all field sampling bottles as directed.

b. Supply and prepare resin cartridges for field sampling.

c. Validate cleanliness of resin cartridges.

d. Determine compound recovery from resin cartridges.

4.2.1 Method Detection Limit

a. Prepare a set of seven samples of standard analytes (unlabelled standard compounds) and analyze according to the procedures in Appendix 2.

b. All concentration calculations will be made according to the method defined in Appendix 2, with final results expressed in nanograms per liter using volume

of the original sample as 45 liters.

4.2.2 Receive and Extract Environmental Samples

a. Ship and receive all sample bottles, resin cartridges and coolers.

b. Receive and handle samples under the chain-of-custody procedures described in Appendix 3, and extract SEP-PAK cartridges as described in Appendix 2.

4.2.3 Analysis of Organic Components in Prepared Fractions

Analyze aliquots prepared in Section 4.2.2 by fused silica capillary GC/MS techniques as given in Appendix 2.

4.2.4 Identification of Organic Components

Identify all PAH and Phenolic compounds (Section 4.3), including isotopes, in the aliquots analyzed in Section 4.2.3.

4.2.5 Quantitation of Identified Components

a. Determine response factors with respect to the quantitation internal standard (d_{10}-anthracene) for the labeled field standards and the labeled laboratory standards which are used for the recovery measurements.

b. Determine response factors with respect to the quantitation internal standard (d_{10}-anthracene) for the carcinogenic PAH and other PAH standard compounds listed in Section 4.3

c. Quantitate the components identified in Section 4.2.4 by the internal standard method, stipulated in Appendix 2 and using the response factors determined above.

d. Two criteria must be satisfied to verify the identifiction of an unknown component as one of the standard compounds: (1) elution of the unknown component at the same GC relative retention time as the standard compounds, and (2) correspondence of the unknown component and standard compound mass spectra. For establishing correspondence of the GC relative retention time (RRT), the unknown component RRT must compare within a 95% confidence interval of the RRT of the standard compound. For reference, the standard must be run on the same shift as the sample. The RRT will be assigned by using extracted ion current profiles (EICP) for ions unique to the component of interest. For comparison of standard and unknown component mass spectra, mass spectra obtained on the same shift on the same GC/MS instrument are required. These standard spectra may be obtained from the run used to obtain reference RRTs. The requirements for qualitative verification by comparison of mass spectra are the three EICP peak intensities of ions specified by EPA must agree within plus or minus 20% with the ratios of the relative intensities between the standard and unknown component ions. When GC/MS computer data processing programs are used to obtain the sample component spectrum, both the processed and the "raw" spectra must be evaluated. If a spectral interference is suspected, additional masses should be investigated.

4.3 Unlabelled and Isotopically-Labelled PAH and Phenolic Compounds to be Identified and Quantitated

Tables 4.1 and 4.2 list the PAH and Phenolic organic compounds that must be identified and quantitated.

Standard compounds (Table 4.2) are carcinogenic and other PAH compounds of interest, including certain priority pollutants for which unlabeled authentic material is available. Accurate response factors and relative GC retention times will be determined for these compounds by reference to the internal standard d_{10}-anthracene. Reference mass spectra will be recorded for subsequent comparison with those of unknown components.

Table 4.2 lists the isotopically-labeled compounds for use as field standards (i.e., added to tne resin in the sampling cartridges), as laboratory standards (i.e., added to the sample prior to extraction) and as the internal standard for quantitation and measurements of relative retention times (i.e., d_{10}-anthracene).

Table 4.1: Standard PAH and Phenolic Compounds For Identification and Quantitation

a. Carcinogenic PAH

Compound	Chemical Abstract Service Registry No.	Method Detection Limit (ng/l)
benzo(a)anthracene	(56-55-3)	5
benzo(b)fluoranthene	(205-99-2)	5
benzo(j)fluoranthene	(205-82-3)	5
benzo(ghi)perylene	(191-24-2)	5
benzo(a)pyrene	(50-32-8)	1.5
chrysene	(218-01-9)	5
dibenz(a,h)anthracene	(53-70-3)	1.5
indeno(1,2,3-cd)pyrene	(193-39-5)	5
quinoline	(91-22-5)	5

b. Other PAH

Compound	Chemical Abstract Service Registry No.	Method Detection Limit (ng/l)
acenaphthene	(83-32-9)	5
acenaphthylene	(208-96-8)	5
acridine	(260-94-6)	5
Anthracene	(120-12-7)	5
benzo(k)fluoranthene	(207-08-9)	5
2,3-benzofuran	(271-89-6)	5
benzo(e)pyrene	(192-97-2)	5
benzo(b)thiophene	(95-15-8)	5
biphenyl	(92-15-8)	5
carbazole	(86-74-8)	5
dibenzofuran	(132-64-9)	5
dibenzothiophene	(132-65-0)	5
2,3-dihydroindene	(496-11-7)	5
fluoranthene	(206-44-0)	5
fluorene	(86-73-7)	5
indene	(95-13-6)	5
indole	(120-72-9)	5
1-methylnaphthalene	(90-12-0)	5
2-methylnaphthalene	(91-57-6)	5
naphthalene	(91-20-3)	5
perylene	(198-55-0)	5
phenanthrene	(85-01-08)	5
pyrene	(129-00-0)	5

Table 4.2: Isotopically-Labeled Standards For PAH and Phenolic Analysis

		Method Detection Limit (ng/l)
a)	**Field Standards**	
	D_8 - maphthalene	5
	d_{10} - phenanthrene	5
	d_{10} - pyrene	5
	d_{12} - benzo(a)pyrene	1.5
b)	**Laboratory Standards**	
	1 - fluoronaphthalene	5
	d_{10} - acenaphthene	5
	d_{12} - chrysene	5
	d_{12} - benzo(a)anthracene	5
c)	**Internal Standard**	
	D_{10} - anthracene	5

4.4 Quality Assurance/Quality Control

All quality assurance procedures prescribed will be strictly adhered to by the Contractor. Records documenting the use of the protocol will be maintained and reported in accordance with Appendix 3.

The Contractor will establish quality control procedures as outlined in Appendix 3 which include not less than 10% duplicate sample analysis, 100% isotope spiked sample analysis, 10% laboratory solvent blanks, and 5% method blanks. GC/MS analyses of field samples as well as QC samples must be carried out according to the schedules in Appendix 2, Table 6.3. Additionally, the Contractor will perform instrument calibration (by "hardware tune") and performance audits to include: decafluoro triphenylphosphine (DFTPP) and calibration standards for response factors, retention times and mass spectra. The Contractor will also include periodic use of his own auditing procedures designed to assure that the operating parameters of the equipment are acceptable and that procedures for sample receipt through data reporting produce reliable data as described by the methods given in Appendix 2. "Reliable data" will be defined as those data falling within the limitations set forth under Appendix 3.

how many conc. levels

After award of the contract and before the first samples are analyzed, the Contractor will determine the analytical method detection limits (or provide analytical data to satisfy the method detection requirement of this protocol). The Contractor will perform seven (7) analyses of one standard mixture in which

all of the compounds are present at 1 - 5 times the required detection limit concentrations (see Appendix 3). These analyses will be performed using the instrumental conditions and methods in Appendix 2.

The Contractor will be responsible for any handling or processing required for the receipt of sample shipments, including pick-up of samples from the nearest express carrier service within the Contractor's geographical area.

The Contractor will be responsible for completing and returning laboratory and chemical analysis data within 21 days of taking the samples.

The Contractor will be required to prepare, after contract award but before analysis of samples, a quality assurance project plan containing the following:

- Project title page, with provisions for signature
- Table of content
- Brief description of project
- Project organization and designated responsibilities
- Quality assurance objectives for PAH and phenolic data, method detection limits, precision and accuracy, completeness and comparability
- Sampling procedure, including SEP-PAK preparation
- Sample transportation and custody
- Calibration procedures, references and frequency
- Analytical methods

- Data reduction, analysis, validation and reporting
- Internal quality control checks and frequency
- Quality assurance performance audits, system audits and frequency
- Quality assurance reports
- Preventive laboratory instrument maintenance procedures and schedules
- Specific procedures used in routinely assessing data precision and accuracy
- Corrective action procedures and responsibilities for out-of-control data

5.0 APPENDIX 1: FIELD SAMPLING

5.1 Preparation For Field Sampling

In addition to the equipment implied in this protocol, the laboratory will also be responsible for ordering, receiving, purchasing and cleaning field sampling equipment (see Table 5.1) including making any modifications to this equipment as required.

Table 5.1: Sampling Equipment to be Ordered by Contractor

C-18 SEP-PAKS	- Waters Corporation
Polypropylene Coupling	- Alltech Associates Part # 200-16
Male Luer	- Alltech Associates Part #200-19
Teflon Tubing (1/8" O.D.X 1.5mm) +End Fitting	- Alltech Associates Part # C-204
Male Needle Lock to Male Needle Lock	- Alltech Associates Part # 8974

Removing a sample from its environment can cause changes due to light sensitivity, changes in temperature, or microbiological action. These and other changes to the sample's chemical composition must be minimized through storage of samples in amber or foil-covered containers, maintaining samples at or near 4 degrees Centrigrade as soon

after receipt as possible, and reducing holding times by processing samples as soon as possible after collection. These measures will be in addition to coordinating the laboratory analytical sample processing with the field collection activities.

Samples will be collected using a Teflon manifold sampling system that continuously samples the groundwater, absorbs the dissolved organics away from the water, and concentrates the organic analytes on macroreticular resin. The macroreticular resin cartridge will be protected from direct light by wrapping the cartridge with aluminum foil.

Water samples from the area will be broadly classified into two groups for sampling purposes: drinking water samples and other aquifer water samples. Contaminant concentrations can range from parts per thousand to parts per trillion or less.

5.2 Resin Cartridge Preparation

The macroreticular sample concentration cartridge (SEP-PAK, a C_{18} filled, small capacity resin cartridge manufactured by Waters Corporation) must be conditioned before it can be used for sampling, recovery efficiencies and method detection limit studies.

Preparation of the resin cartridges consists of flushing each with 4.0 ml HPLC-grade methanol then 10. ml HPLC-grade

water using a 10.0 ml Luer Lock glass syringe. Each resin cartridge system consists of two SEP-PAKS connected in series by a male Luer Lock (see figure 5.1).

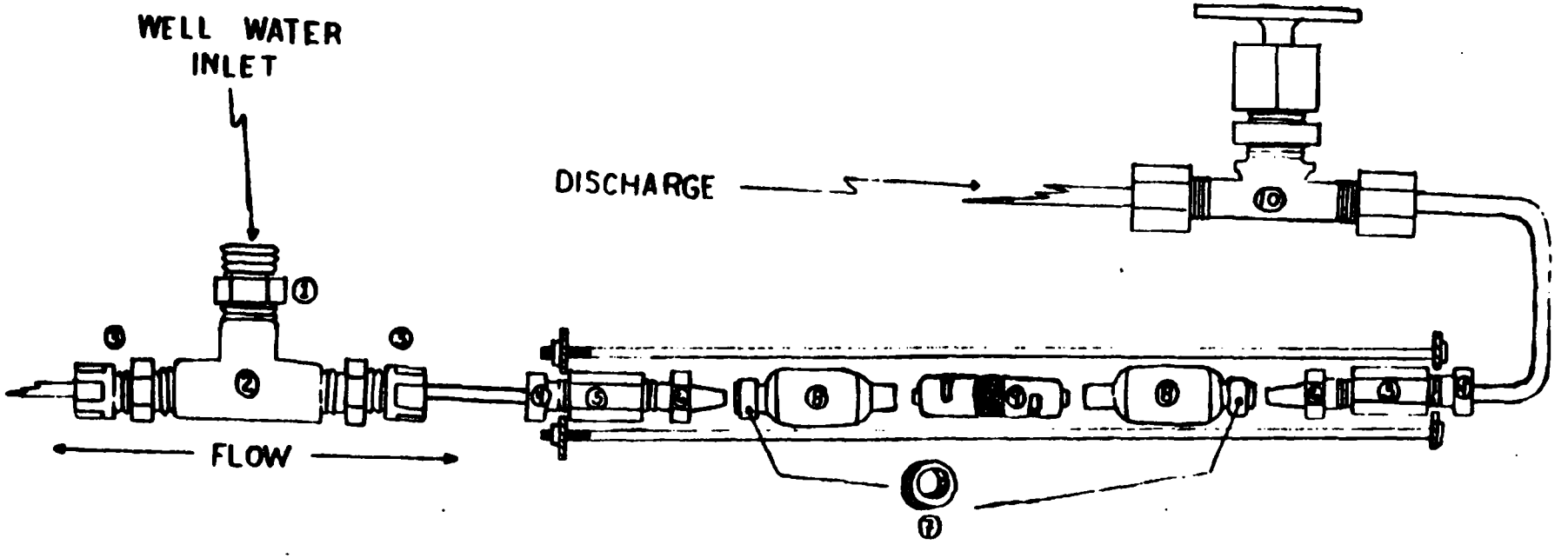
One of the cartridges is spiked with isotopically-labelled field standards (Table 4.2.a) in the laboratory. The isotope spike level should be similar in concentration to the native compounds being analyzed. The spiking is accomplished by syringe injecting (using a plunger in needle microliter syringe) the isotope mixture onto the inlet head of one of the SEP-PAKs. A gentle vacuum is placed on the outlet side of the SEP-PAK to help draw the isotope mixture into the resin. After the SEP-PAK is spiked, organic free water (approx 5 ml) is transfered from a pipet into the SEP-PAK in a continuous fashion while maintaining vacuum.

The spiking procedure is conducted in an identical fashion as described above for unlabeled standards used during the method validation process (i.e., recovery efficiencies and method detection limit) and on-going quality control (i.e., method check analysis). All samples will be extracted according to the procedures given in Appendix 2, Section 6.2.

5.3 Field Sampling Procedure

Sample collection is a vital part of this project and the protocol used should provide samples which will neither be altered through the sampling procedure nor contaminated

Figure 5.1: SEP-PAK Cartridge Pair



1. 1/8" x 1/8" Teflon Nipple
2. 1/8" Teflon Pipe Tee
3. 1/8" Tubing x 1/8" NPT Teflon Male Connector
4. 1/8" O.D. x 1.5mm I.D. Teflon Tubing + End Fitting
5. Polypropylene Coupling
6. Tefzel Male Luer
7. Stainless Steel Sleeve
8. C_{18} SEP-PAK
9. Male Needle Lock to Male Needle Lock
10. 1/8" O.D. Tube x 1/8" O.D. Tube Needle Valve

during sampling. Therefore, all field sampling activities will be directed by written standard operating procedures, samples will be carefully tracked by chain-of-custody, and all field activities, data, and observations will be carefully and accurately recorded in a bound field notebook.

The field sampling system (consisting of two SEP-PAK cartridges in series) is connected to the well (before chlorine and fluoride addition to the water supply) by an all-Teflon manifold. The manifold attaches to a stainless steel sleeve that extends into the center of the well head pipe, allowing the water sample to be drawn from near the center of the pipe. The Teflon manifold is designed to collect samples in duplicate by splitting sample flow with a tee to two SEP-PAK cartridge pairs. Two Teflon needle valves (one on each side of the tee) are used to control water flow through the SEP-PAK cartridges. A flow rate of approximately 30 ml/min is maintained (do not exceed 35 ml/min) through the cartridges during sample collection. The flow from each SEP-PAK cartridge pair is collected in a tared carboy. At the end of the sampling period, the water volume sampled is determined by weighing the carboy and water. At the completion of sampling, the SEP-PAK cartridges are wrapped in foil and refrigerated at 4°C until extraction (see Section 6.2).

The amount of PAH and phenloic contaminants in the other acquifer wells, excluding the municipal supply wells where

the contaminant levels are normally not detectable, can vary from parts per thousand to parts per trillion or less. Because the concentration of contaminants varies considerably, the total volume of water sampled from drinking water wells (approximately 45 liters) will normally be larger than the other acquifer wells (approximately 2 to 45 liters).

5.4 Resin Cartridge % Recovery Determination

The procedure for determining recovery will be based on the analysis of seven cartridges spiked with a menu of compounds (isotopically and non-isotopically labeled). The compounds selected for spiking are listed in Section 4.3. The spiking concentration per compound will be approximately 5 times the detection limit reported in Section 4.3.

The spiking technique is identical to that described in Section 5.2 These spiked cartridges are carried through the extraction procedures and quantitated as specified in Appendix 2. The concentration of these spiked compounds when compared to the concentration of d_{10}-anthracene added to the final extracts allows a percent recovery to be determined for each compound. Calculations will be conducted according to recovery efficiencies described in Appendix 2, section 6.4.

5.5 Determination of Method Detection Limit

Information about the lowest quantity of analyte that can be

reliably detected by an instrumental technique is essential to interpreting any analysis. To ensure that the estimate of the method detection limit is a good estimate, an accurate lower analyte concentration estimate will be made from the recovery data determined in Section 5.4 above.

Seven cartridges will be spiked with the list of standard compounds in Section 4.3, Table 4.1. The analyte spike concentration added to the cartridge before extraction will yield a final fraction concentration between one and five times the estimated method detection limit.

The initial calculated method detection limit, as determined above, is tested by spiking a cartridge (as described in Section 5.2) at the calculated method detection limit and processing the sample as described in Appendix 2. It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with the analysis of all seven spiked resin cartridges.

When the desirable method detection limit has been determined experimentally, the standard deviation of the seven replicate measurements is calculated as described in Appendix 3, section 7.5.

6.0 APPENDIX 2: ANALYTICAL METHODS

6.1 General

Meticulous care will be taken at all stages of this project to insure that sample integrity is preserved by maintaining acceptable laboratory practices for trace organic analysis.

It is particularly important that all equipment and laboratory glassware used in this project be scrupulously cleaned and the integrity of the equipment and glassware be verified through appropriate QA/QC procedures. The analysis of PAH and phenolic compounds at the low part per trillion range requires special measures to prevent contamination. The following list of procedures will minimize contamination problems.

6.1.1 Solvents

Freshly distilled nanograde solvents are used for standard solution preparation and sample extraction. The ditillation column is packed with 90 cm of glass helices.

6.1.2 Procedure for cleaning laboratory glassware

- Wash glassware thoroughly in hot MICRO^{TM} detergent water.
- Rinse the glassware thoroughly in hot tap water.
- Soak the glassware overnight in chromic acid.
- After the chromic acid soak, drain glassware well and rinse thoroughly with ultra-pure deionized water.
- Heat glassware at 625^{o}F for one-hour (do not place calibrated tubes, vials and receivers in the oven at 625^{o}F).*

- Allow glassware to cool in an area where they are protected from sources of contaimination.
- Change filters and beds as required on the ultra-pure water system to maintain QA/QC criteria.

* Note: Calibrated tubes, vials and receivers are instead rinsed with nanograde acetone and then nanograde methylene chloride.

6.2 SEP-PAK Cartridge Sample Extraction

Each SEP-PAK cartridge pair, prior to sampling, is spiked with a solution of isotopically-labeled field standards (see Appendix 2, Section 5.2). The solution of isotopically-labeled laboratory standards (see section 4.3, Table 4.2.b) is spiked on the cartridge pair in an identical fashion to monitor the laboratory extraction procedure.

Prepare a sodium sulfate micro-drying column and pre-rinse the column, sodium sulfate (rinsed with distilled THF, 20 ml/g, and conditioned at 400°C for 4 hrs.) and glass wool with 10 ml acidified THF.

Extraction of the absorbed organic materials from the resin is accomplished by flushing the cartridge pair with tetrahydrofuran (THF) containing 0.1% (V/V) concentrated hydrochloric acid (HCL).

The SEP-PAK cartridge pair is attached to a 20-ml Luer Lock syringe. The syringe is used to slowly flush the cartridges

with 15 ml of acidified THF which is immediately passed through the micro-drying column to remove water. The dried THF extract is collected in a 50-ml (graduated in 0.5 ml increments) conical screw cap tube. The micro-drying column is rinsed with 5 ml of acidified THF.

Gently warm the conical tube with a heat gun and reduce the THF solvent volume under a gentle stream of high purity nitrogen. Concentrate to an apparent volume of 0.5 ml, rinse the tube walls with two 0.2 ml rinses of acidified THF using a 0.5 ml syringe. Quantitatively transfer the THF extract into a 5-ml conical centrifuge tube with 0.1 ml graduations. Rinse the walls of the concentrator tube with two 0.2 ml THF rinses. Quantitatively transfer the rinses to the centrifuge tube. Place in refrigerator until GC/MS analysis.

Immediately prior to GC/MS analysis, remove the extract from the refrigerator and reduce the volume of the extract to approximately 0.2 ml with a gentle stream of nitrogen while warming the centrifuge tube with a heat gun. Add d_{10}-anthracene internal standard to the extract. Solvent exchange the THF by adding 0.2 ml cyclohexane. Continue reducing the volume of the extract to 0.1 ml. [Note: The cyclohexane solvent exchange is necessary to remove materials that cause plugging of narrow bore capillary columns.]

Centrifuge the tube to settle floculant if necessary. Finally, inject 2.0 microliters of the sample extract into the GC/MS.

6.3 Analysis by Fused Silica Capillary Gas Chromatography/Mass Spectromity (GC/MS)

Extracts prepared as described in Section 6.2 above will be analyzed by GC/MS using direct coupled fused silica capillary column (0.25 mm i.d. bore) to provide maximum resolution of the components, and by continuous repetitive acquisition of complete full-scan mass spectra (35-450 amu). Operating conditions vary from one system to another, therefore, each analyst must optimize the conditions for each system to achieve maximum sensitivity. This generally requires an increase in electron multiplier voltage to increase sensitivity.

Tables 6.1 and 6.2 summarize recommended gas chromatographic column materials and operating conditions for two GC/MS instruments. Suggested analytical conditions for determination of the pollutants amenable to this technique are given in these Tables. Operating conditions vary from one system to another, therefore, each analyst must optimize the conditions for each system.

Evaluate the gas chromatographic/mass spectrometer system performance each day that it is used for analysis of samples or blanks by examining the mass spectrum of DFTPP. Preparation of the instrument for analysis will consist of running a self-tuning proram with DFTPP to optimize the mass spectrometer operating parameters and to calibrate the mass axis.

If the system performance criteria are not met, the analyst

must tune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards are analyzed. Analyze a mixture of standard compounds (see Table4.1) and labeled compounds (see Table 4.2) to develop response factors for each component. Following analysis of standard mixtures, extracts will be analyzed interspersed with appropriate positive and negative standards (see Table 6.3) by injecting a 2 ul aliquot onto the GC/MS column.

6.4 Calibration

In order to verify the linearity of the GC/MS procedures, prepare a solution of standard compounds from the standards listed in Section 4.3. Each component should be at a concentration of 1.00 mg/ml and this solution will be used to prepare calibration solutions at concentrations of 50, 25 and 0.5 ng/ul. Assemble the necessary chromatographic and mass spectrometric equipment and establish operating parameters equivalent to those indicated in Table 6.1 and 6.2.

By injecting calibration standards, establish the linear range of the analytical system and demonstrate that the analytical system meets the method detection limits of Table 4.1.

A calibration curve encompassing the concentration range of interest is prepared for each compound to be analyzed. Once the system has been calibrated, the calibration must be varified at least once each 12 hours. If the mean percent change is greater than the precision analysis process (see

Appendix 3, Section 7.8.2) the system must be recalibrated using a 3-point calibration curve for each compound.

Table 6.1: Instrument Parameters: GC/MS Procedure for Analysis of Polynuclear Aromatic Hydrocarbons and Phenolics

Gas Chromatograph

Hewlett Packard 5840 (with HP7671A Autosampler optional)

Column	: 30m x 0.20mm SE-54 fused silica capillary directly coupled to MS

Injection

Mode	: splitless
Sweep Initiation @ 0.5 minutes	
Sweep Flow	: 40 ml/min. helium
Carrier Flow	: 1cm/sec. linear velocity
Injection volume	: 2 ul

Temperatures

Injector	: 250°C
Temp. 1	: 40°C for 3 minutes
Tamp	: 8°C/minute
Temp. 2	: 300°C
Interface Temp.	: 275°C

Mass Spectrometer

Hewlett Packard 5985B GC/MS	
Electron Impact Mode	: 70 or performance equivalent eV
Mass Range	: 35-450 amu
Delay	: 7 minutes
Samples/point	: 3
Threshold	: 14
Multiplier Voltage	: 1800

Data System

Hewlett Package 21MX-E	
Disc Drives	: HP7906 (20M byte), HP7920 (80M byte) or performance equivalent
Tape Drive	: Kennedy 9300 9-track dual density or performance equivalent

Table 6.2 Instrument Parameters: GC/MS Procedures for Analysis of Polynuclear Aromatic Hydrocarbons and Phenolics

Gas Chromatograph

Finnegan Model 9610

Column	: 30m x 0.25mm SE-54 Fused Silica Capillary Column directly coupled to the MS ion source

Injection

Mode	: splitless
Sweep Initiation	: 1 min
Sweep Flow	: 5cc/min
Split Flow	: 40cc/min
Injection volume	: 2 ul

Temperatures

Injector	: 250°C
Temp 1 (@ injection)	: 28°C
Temp 1 (after injection)	: 80°C for 4 min
Ramp	: 9°C/min
Temp 2	: 310°C for 30 min
Interface Temperature	: 270°C

Mass Spectrometer

Finnigan Model 4000	
Electron Impact Mode	: 70ev
Mass Range	: 35-450amu
Ionizer Temp	: 260°C
Multiplier voltage	: 1000-1100
Dynode voltage	: 3000
Emission current	: 0.45 milliamps
Scan Time	: 0.5 seconds/scan

Data System

Computer	: Data General Nova 4
Software	: INCOS
Magnetic Tape Storage	: Finnigan/Perkin-Elmer

Table 6.3 Schedule for PAH and Phenolic Analysis by GC/MS

Sequence	Type of Sample
1	Tune instrument
2	*Standard (mixture in Table 4.1)
3	*Blank solvent
4	Sample
5	Sample
6	*Method spike (mixtures in Table 4.1 and Table 4.2; see Section 7.5.6).
7	Sample
8	Sample
9	*Duplicate (not < 10% Duplicate Analysis)
11	*Standard (mixture in Table 4.1)

* Quality Control Sample

6.5 Data Interpretation, Quantitation and Evaluation

Once the mass spectral data collected from a GC/MS run has been evaluated, accepted and archived, interpretation of the data will proceed in order to identify the components in Tables 4.1 and 4.2. Data interpretation will be achieved manually by an expert mass spectrometrist with computer assistance in the form of special algorithms and library search routines. The computer assistance used may include:

(1) total ionization chromatograms;

(2) specific mass chromatograms:

(3) automatic background subtraction;

(4) Biller-Biemann flagging algorithms;

(5) mass spectral subtractions;

(6) reverse library searching algorithms;

and (7) retrieval of authentic library spectra.

However, although such computer techniques are an extremely valuable asset in the data interpretation process, they are, unfortunately, not infallable for complex mixture analyses and, therefore, specific mass spectral identifications will be made after the mass spectrometrist has inspected the raw data.

For certain compounds such as the standard compounds for which relative response factors are known, quantitation will be achieved using the method provided below.

A total ion chromatogram will be plotted for each acquisition, then single ion chromatograms will be generated for the

characteristic ions for each compound being quantitated.

Areas will then be obtained for any peak with a retention time falling within ± 0.02 RRT units of the most recent standard run. Confirmation of identity will be based on the presence of the EPA selected ions (1-3 ions) for the individual compound, and all ions must maximize within three scans of each other. Furthermore, the ions must meet spectral integrity criteria for relative ratios (± 20%). The areas under each characteristic ion peak are used to determine the extract concentration. The areas are compared to the internal standard intensity based on the following formula:

$$\text{Concentration}_{unk} = \frac{(\text{Area}_{unk})\ (\text{Conc}_{IS})}{(\text{Area}_{IS})\ (RF_{unk})\ (Vo)}$$

Concentration = Concentration of pollutant in original sample in ng/l

where: unk = component being quantitated

IS = internal standard, d_{10}-anthracene

Vo = Volume of the original sample in liters

RF = response factor for the particular compound

$$RF = \frac{(\text{Area}_S)\ (\text{Conc}_{IS})}{(\text{Area}_{IS})\ (\text{Conc}_S)}$$

$Area_S$ = Integrated area of characteristic ion for the pollutant standard

$Area_{IS}$ = Integrated area of characteristic ion for d_{10} - anthracene

$Conc_{IS}$ = Amount (ng) of internal standard, d_{10} - anthracene

$Conc_S$ = Amount (ng) of pollutant standard

Recovery efficiencies will be determined from the isotopically-labeled standards added to each sample. These spiked materials will be carried through the extraction procedures and quantitated. The concentration of these spikes when compared to the concentration of the spike added to the sample allows a percent recovery to be determined for each labeled component:

$$\text{Percent Recovery} = \frac{\text{Concentration of Spike Measured}}{\text{Concentration of Spike Added to Sample}} \times 100$$

In addition, a laboratory method spike (see Section 7.5.6 Method Check Analysis) will be analyzed with each set of samples (see Table 6.3). Solutions of standard compounds and isotopically-labeled compounds (see Section 4.3) will be taken through the procedures specified in Section 6.2 and the recovery efficiencies will be calculated for each component.

7.0 APPENDIX 3: QUALITY ASSURANCE/QUALITY CONTROL PROGRAM

7.1 General

The primary function of the QC program outlined here is the definition of procedures for the evaluation and documentation of analytical methodologies and the reduction and reporting of data. The objective of this QC Appendix is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any analysis. In the instances where methodologies are existing, specific quality control procedures are provided for method documentation. For cases where new methodologies must be established, a guide specifying the minimum method validation procedure, quality control, and documentation requirements is presented. Samples analyzed under this project are analyzed only after the methods have met the minimum performance and documentation requirements described in this document. Each bidder is asked to provide documentation in writing that demonstrates a part per trillion detection limit QC program is currently in practice, or how the bidder plans to implement a QC program.

Standard laboratory practices for laboratory cleanliness as they apply to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and

gases should also be adhered to. For additional guidelines regarding these general laboratory procedures, please see Sections four and five of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, ISEPA Environmental Monitoring & Support Laboratory, Cincinnati, Ohio, March, 1979.

7.2 Chain-of-Custody and Document Control Procedures

7.2.1 Sample Control

An essential part of this project is that samples gathered be controlled. To accomplish this, the following chain-of-custody and document control procedures have been established.

7.2.2 Sample Identification

Each sample shall be labeled with a tag containing the sample number and sample description to identify the contents. Additionally, the sample number shall be marked on the outside of any special packaging container to facilitate identification.

7.2.3 Chain-of-Custody Procedures

The possession of samples must be traceable from the time the samples are collected until the results are reported. To maintain and document sample custody, the chain-of-custody procedures described here are followed. A sample is under custody if:

a. it is in your actual possession, or

b. it is in your view, after being in your physical possession, or

c. it was in your possession and then you locked or sealed it up to prevent tampering, or

d. it is in a secure area.

To assure custody of samples during transport and shipping, each sample within a packing container will be recorded on a chain-of-custody record. Each sample number will be recorded and the number of containers shipped will be recorded on the sheets. Also other information regarding the project, samples (or shipper if returning empty bottles), method of shipment and signature and date will be recorded on the sheet. The original custody sheet will be placed inside the package (protected from damage) and the sample containers, shipping boxes, coolers or other packages will be sealed.

Upon receipt of samples in custody, inspect the package and note any damage to the sealing tape or custody seals. Note on the custody record or logbook that the seals or locks were intact upon receipt if no tampering or damage appears to have occurred. Open the package and verify that each item listed on the sheet is present and correctly identified. If all data and samples are correct, sign and date the "received by Laboratory by" box. In the event errors are noted, record the discrepancies in the remarks column (initial and date each comment) then sign the

chain-of-custody record.

7.2.4 Laboratory Document Control

Accountable documents used by contract laboratories shall include logbooks, chain-of-custody records, lab sample and bench sheets and other data sheets described in the "Quality Assurance and Document Control Procedures" program. All accountable documents are under the supervision of a designated document control officer assigned by the Contractor to maintain control of confidential information.

7.2.5 Logbooks

All observations and results recorded by the laboratory but not on preprinted data sheets are entered into permanent laboratory logbooks. Data recorded are referenced with the project number, date and analyst's signature at the top of the page.

7.2.6 Corrections to Documentation

All documentation in logbooks and other documents shall be in ink. If an error is made in a logbook assigned to one individual, that person may make corrections simply by crossing a single line through the error and entering the correct information. Changes made subsequently are dated and initialed. Corrections made to other data records or non-personal logbooks are made by crossing a single line through the error, entering the correct information and initialing and dating the correction.

7.2.7 Consistency of Documentation

Before releasing analytical results, the laboratory assembles and cross checks the information on sample tags, custody records, lab bench sheets, personal and instrument logs and other relevant data to ensure that data pertaining to each particular sample is consistent throughout the record.

7.2.8 Document Numbering and Inventory Procedure

In order to provide document accountability of the completed analysis records, each sample in this project is inventoried and each data generator (analyst) is responsible for ensuring that all documents generated (including logbook pages, bench sheets, computer file ID's, mass spectra, chromatograms, custody records, etc.) are placed in the file for inventory.

7.3 Sample and Laboratory Data Logging

7.3.1 Introduction

This section describes examples of laboratory data sheets used to document sample preparation, sample analyses, and data calculation. Each data sheet is described with each element defined within a form. It is important that laboratory data sheets be accountable when the project is completed (see labortory Document Control section 7.2.4).

7.3.2 Sample Log Sheet

Sample log sheets should be designated to maximize

internal controls over the activities that are performed on the samples. The sheets should be designed to follow the flow of the analytical methodology and document the fact that the samples were taken through the appropriate steps. Each sample received for organics analysis is assigned a laboratory sample sheet.

7.3.3 Personal Logs

Personal logbooks are maintained to supplement the data logged on the particular lab sheets. Detailed records of anomalies in a sample or procedure and actions to correct those problems are especially important.

7.3.4 Organics Laboratory Chronicle

This form is completed by the laboratory and is used to record the dates the samples are extracted and any problems associated with extraction.

7.3.5 Identification/Quantitation Work Sheet

Identification/quantitation work sheets are raw data sheets used to organize data processing.

7.3.6 GC/MS Instrument Operations Log

Each instrument has an operations log associated with it. The operations log contains information concerning the instrument's performance, operating conditions, maintenance, and use. The GC/MS performance log shall contain information on performance criteria.

7.3.7 Preparation of Standards Log

The preparation of standards shall be documented on the Preparation of Standards log form. Information on the concentration, solvent, and analyst will be provided on this form.

7.4 Method Detection Limit

Information about the lowest quantity of analyte that can be reliably detected by an analytical technique is essential to interpreting any analysis.

The method detection limit (MDL) refers to samples processed through all the steps comprising an analytical procedure. The MDL is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero and is determined from replicate analyses of a sample of a given matrix containing the analyte.

The procedure for determining the MDL is based on the analysis of seven samples of the matrix containing the analyte. A laboratory standard of the analyte in the matrix is prepared at a concentration at least equal to or in the same concentration range as the estimated MDL.

It may be economically and technically desirable to evaluate the estimated MDL before proceeding with the analysis of the seven aliquots. This will prevent repeating the entire

procedure and ensure that the MDL determination is being conducted at the correct concentration.

If the sample is not in the correct range, the MDL must be reestimated and seven new aliquots of the sample matrix processed. The standard deviation of the seven replicate measurements is calculated and the MDL is computed as:

$$\underline{MDL} = t_{(N-1,\ 1-a\ =\ .99)} \times S_c$$

where:

$$\underline{t}_{(N-1,\ 1-a\ =\ .99)} \times S_c$$

is the student's t value for a one-tailed test at the 99% confidence level with N-1 degrees of freedom. S_c is the standard deviation of the seven replicate analyses. Confidence-interval estimates for the MDL are computed using percentiles of the chi square over degrees of freedom distribution (X^2/df). The 95% confidence limits for the MDL are:

$$\underline{UCL_{MDL} > MDL > LCL_{MDL}}$$

$$P_{.025} \qquad P_{.975}$$

where the percentiles values are obtained from the X^2/df distribution for the associated degrees of freedom (df=6).

$$LCL_{MDL} = 0.64\ MDL$$

$$UCL_{MDL} = 2.20\ MDL$$

The confidence limit expression reduces to where LCL_{MDL} and UCL_{MDL} are the lower and upper 95% confidence limits of the MDL based upon the analysis of seven aliquots.

For additional guidelines regarding these general laboratory procedures, please see "Definition and Procedure for the Determination of the Method Detection Limit Revision 1.12"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, January, 1981.

7.5 Laboratory Quality Control

This section outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with this project. These QC operations are as follows:

- Documentation of GC/MS Mass Calibration and Abundance Pattern.
- Documentation of GC/MS Response Factor Stability.
- Internal Standard Response and Retention Time Monitoring.
- Standard Response Monitoring.
- Methods Blank Analysis.
- Isotope Spike Analysis.
- Duplicate Sample Analysis.

7.5.1 DFTPP Ion Abundance Criteria

Each day the GC/MS system must be calibrated as described in Method 625. Documentation of the calibration must be provided in the form of a bar

graph plot and as a listing. DFTPP has to be injected to meet this criterion. Post-acquisition manipulation of abundances is not acceptable.

7.5.2 Calibration Standards

The GC/MS system must be initially calibrated at a minimum of three concentrations to determine the response factors using standards (Section 4.3) as described in Method 624 or 625. Once the system has been calibrated, the calibration must be verified at least once each 12 hours. If the mean percent change for the calibration check compounds is greater than ten percent, the system must be recalibrated using a 3-point calibration curve for each compound.

$$\text{Percent Change} = \frac{RFv - RFc}{RF_c} \times 100\%$$

RFc = response factor from initial calibration

RFv = response factor from current verification check standard

Response factors for all compounds are to be recorded each day using for initial calibration data and for check standards data.

7.5.3 Internal Standard Response and Retention Time Monitoring

Internal standard response factor and retention time must be evaluated immediately after or during data acquisition. This is done by: after three calibration standards runs have been made, calculate the mean values for retention time and extracted ion current profile (EICP) area. If the retention time for any internal standard of a

subsequent run changes more than 5 seconds from this mean, the chromatographic system must be inspected for malfunctions and corrections made as required. If the EICP area of a subsequent run changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. Retention time and EICP area records may be maintained in the form of control charts by the laboratory as part of its internal quality control.

7.5.4 Isotope Recovery

Isotope standards are added to all resin cartridges before entering the field for sample collection to monitor resin retention efficiency and added to all resin cartridges prior to extraction to monitor laboratory performance. Isotope Recovery must be evaluated for acceptance by determining whether the measured concentration falls inside the limits.

$$\text{Percentage Isotope Recovery} = \frac{Q_d}{Q_a} \times 100\%$$

where: Q_d = quantity determined by GC/MS, and

Q_a = quantity added to the sample.

Treatment of isotope recovery information is as follows:

(a) If isotope recovery is outside the acceptance limits for a method check analysis (see Section 7.5.6), the sample should be reinjected. If this fails to correct the problem, the analytical system is out of control and must be corrected before continuing. This may mean recalibrating the instrumentation but

it may mean more extensive action. The specific corrective action is left up to the GC/MS operator and/or other qualified personnel.

(b) If isotope recovery is outside the acceptance limits for a sample, this must be noted by so indicating in appropriate portion of the data sheet and contact the Quality Assurance Officer. Isotope spike results must also be reported using and control chart.

7.5.5 Method Blank Analysis

Method blank analyses, must be performed as specified by the method or whenever samples are extracted whichever is more frequent. The method blank is used in all analyses to verify that the determined concentrations do not reflect contamination.

If any contaminants are detected in the blank, the blank value is utilized in the sample calculation of the sample according to the following:

(a) If the concentration in the blank is less than or equal to 1/2 of the method detection limit, the blank value is ignored.

(b) If the concentration in the blank is greater than 1/2 of the method detection limit and is less than or equal to 1/2 the concentration detected in a sample, subtract the concentration in the blank from the concentration in the sample. Record the corrected value and indicate that this has been done.

(c) If the concentration in the blank is greater than 1/2 the method detection limit and if the blank

concentration is greater than 1/2 the concentration detected in a sample, correction is not possible and the compound should be reported as "ND" but indicate this has been done on the data sheet. The cause of this high blank should be determined and corrected before additional samples are analyzed.

7.5.6 Method Check Analysis

Method check analyses will be conducted by spiking SEP-PAK cartridges in the laboratry with unlabeled and isotopically-labeled PAH and Phenolic Compounds to verify the laboratory's continuing ability to perform analyses within the limits identified as acceptable in Section 7.8. These acceptance criteria, established from QC charts, will be based on analysis of method check samples conducted during the method validation process. Deviation by one or more of the standard spike compounds (labeled or unlabeled) from their acceptable values indicates that sample preparation and/or analysis conditions are out of control and that corrective action is required before another set of samples is prepared or analyzed. Because these methods are intended for use by experts, the exact nature of corrective action is not defined here. Once corrective action has been taken, however, a new method check analysis must be performed to verify that the action taken was sufficient to bring the analyses under control.

Percentage recoveries are calculated as follows:

$$\text{Percent Recovery} = \frac{Q_d \times 100\%}{Q_a}$$

where: Q_d = quantity determined by GC/MS, and

Q_a = quantity added to sample.

7.5.7 Duplicate Sample Analysis

Duplicate Sample Analysis must be performed on 1 of each 10 samples. The percent differences (PD) for each component are calculated as follows:

$$PD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100\%$$

where: PD = Percentage Difference

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

The percent difference data will be used to evaluate the long-term precision of the method.

7.6 Method Validation

Initially, an analytical methodology is checked for precision and accuracy before an on-going quality control program is implemented. Precision refers to the degree of random error or the reproducibility of an analytical methodology while accuracy refers to the degree of systematic error or bias of an analytical methodology.

7.6.1 Method Precision

The precision of a methodology is measured as follows. Four sample solutions of varying concentration of the species to be quantitated are analyzed in replicate. The

samples tested consist of a sample of concentration near the sensitivity level of the method, two samples of intermediate concentrations, and a sample near the upper limit of application of the method. Replicate determinations are made of each sample solution in the following order. . . the highest concentration, the lowest concentration and the two intermediate concentrations. This series is repeated seven times. The degree of precision is then measured using the calculated standard deviations of the samples tested. The standard deviation S is calculated using the following equation:

$$S = \sqrt{\frac{n\sum_{i=1}^{n}(x_i)^2 - \left(\sum_{i=1}^{n} A_i\right)^2}{n(n-1)}}$$

(where x_1 are the data, and n is the number of data points)

The resulting statement of precision includes the range of concentrations tested by the methodology and the largest standard deviation.

7.6.2 Method Accuracy

The accuracy of a methodology is measured as follows. Known amounts of the species to be quantitated are added to samples previously analyzed such that the concentration is doubled for a sample near the sensitivity level of the method, and that the concentration of a sample of intermediate concentrations is approximately seventy-five percent of the upper limit of application of the method.

Seven replicate determinations are made of each of the spiked samples. The degree of accuracy is then measured using the calculated percent recoveries of the samples tested. The percent recovery P is calculated using the equations:

$$\bar{X} = \frac{\sum_{i=1}^{n} x_i}{n} \quad \text{and} \quad P = 100 \left(\frac{\text{spiked } \bar{X} - \text{unspiked } \bar{X}}{\text{spike}} \right)$$

(where S_1 are data, and n is the number of data points). The resulting statement of accuracy includes the concentrations of the spiked samples tested and their respective percent recoveries.

7.7 On-going Quality Control

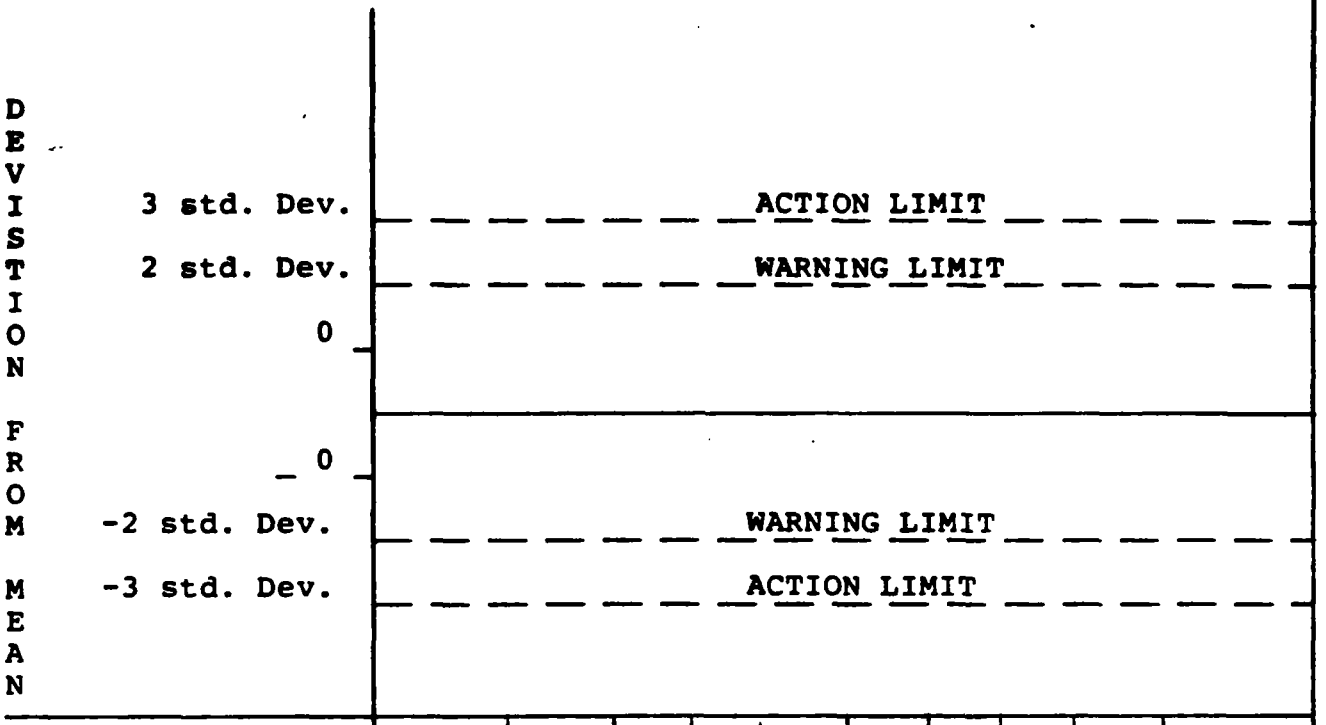
Once the validity of a methodology has been verified, systematic daily checks of precision and accuracy are performed. These checks require the analysis of standards, blanks, duplicate samples and spiked samples. The daily precision and accuracy of a methodology are recorded on quality control charts (see Form 7.1).

The daily verification of the standard curve is performed by analyzing a high concentration and a low concentration standard solution which are within the applicable range of the method. The agreement between the previously constructed standard curve and the current values of the standards tested should be within the precision of the method. Corrective measures are taken if the results indicate otherwise. No data is valid until the precision of the method is obtained.

Sample concentrations must be within the applicable range of the method, i.e., within the standard curve. Those samples exceeding the method's range are diluted appropriately. Alternatively, a new standard curve is constructed to include the higher concentration samples.

The precision of the methodology is documented by replicate analyses if at all possible. Ten percent of the samples tested are split and analyzed in duplicate. The results are to be within the limits of precision established by the quality control charts, otherwise, corrective measures are taken. Similarly, the accuracy of the methodology is documented by the analysis of solutions of known concentration. Ten percent of the samples tested are either spikes, standards, or previously analyzed samples. The percent recoveries should be within the limits of accuracy established by the quality control charts, otherwise corrective measures are taken.

METHOD _____



RUN NO.	1	2	3	4	5	6	7	8	9	10
DATE/TIME										
OPERATOR										
PROBLEM AND CORRECTIVE ACTION										

FIGURE 7.1. A STANDARD QUALITY CONTROL CHART

7.8 Quality Control Charts

The recording of precision and accuracy data on quality control charts allows the determination to be made as to whether a methodology is in control or not in control. The quality control charts also point out the development of trends toward a lack of control and serve as chronological records of performance.

7.8.1 Precision Control Charts

Since precision control charts are constructed from data obtained from replicate analyses, an initial series of duplicate samples are tested. These initial sets of duplicate samples are then used to construct the control charts by using the following equations:

$R_i = 1X_i$ where R_i is the range of duplicate data X_i and X_i

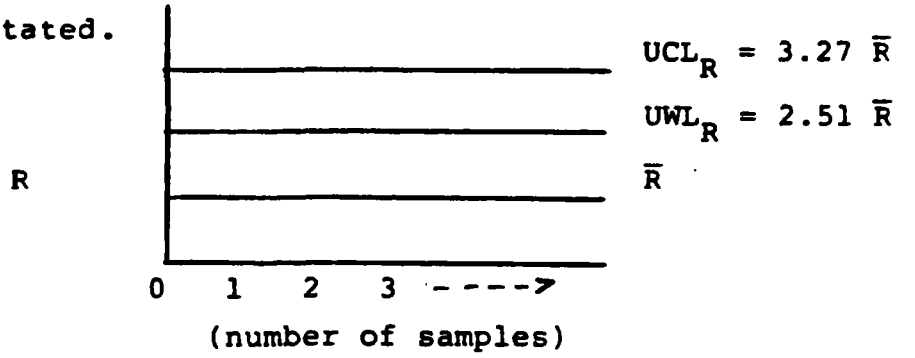
$$\bar{R} = \frac{\sum_{i=1}^{n} R_i}{n}$$ where n is the number of sets of duplicate samples

$UCL_R = 3.27\ \bar{R}$ where UCL_R is the upper control limit

$UWL_R = 2.51\ \bar{R}$ where UWL_R is the upper warning limit (95% confidence level)

Notice that only values of R greater than the detection limit of the method are used to construct the control charts. After plotting $\bar{R}$, UCL_R and UWL_R, subsequent duplicate samples are plotted on the chart. Periodically, the subsequent duplicate samples are included in the recalculation and updating the values of $\bar{R}$, UCL_R and UWL_R, (i.e., the control chart). The method is determined to be out of control if a R_i exceeds the UCL_R. If the method is determined to be out of control, the analysis is

stopped and corrective measures are taken. All data generated while the method was out of control is invalid; reanalysis is required. An example of a precision quality control chart is illustrated below. To be included on the charts is such pertinent information as the method of analysis, the data identities, the chart's preparation date and the species being quantitated.



(number of samples)

7.8.2 Accuracy Control Charts

Since accuracy control charts are constructed from the percent recoveries of standards and spiked samples, an initial series of samples of known concentrations are tested. These initial samples' percent recoveries are then used to construct the control charts by using the following equations:

$$\bar{P} = \sum_{i-1}^{n} P_i$$

where P_i is percent recovery and n is the number of data points.

$$Sp = \sqrt{n \sum_{i=1}^{n} P_i^2 \left(\sum_{i=1}^{n} P_i \right)^2}$$

where P_i is percent recovery, and n is the number of data points.

For standards:

$$P_i = 100 \times \frac{\text{observed concentration}}{\text{known concentration}}$$

$UCL_p = P + 2Sp$ where UCL_p is the upper control limit

$UCL_p = P - 2Sp$ where LCL_p is the lower control limit

For spikes:

$$P_i = 100 \times \frac{\text{observed concentration} - \text{background concentration}}{\text{spike}}$$

$UCL_p = P + 3Sp$ where UCL_p is the upper control limit

$UCL_p = P - 3Sp$ where LCL_p is the lower control limit

Note that the charts are not valid unless at least fifty percent of the data used to construct those charts are within the interval $P \pm Sp$. Also, note that separate charts are constructed for standards and spiked samples due to their different control limits. After plotting P, UCL_p and LCL_p, subsequent standards and spikes samples are plotted on the chart. Periodically, the subsequent standards and spiked samples are included in the recalculation and updating of the values of P, UCL_p and LCL_p, i.e., the control charts. The method is determined to be out of control if a P_i exceeds either control limit or seven consecutive P_i's are on the same side of P. If the method is determined to be out of control, the analysis is stopped and corrective measures are taken. All data generated while the method was out of control is invalid and reanalysis is required. An example of an accuracy quality control chart is illustrated below. To be included on the charts is such information as the method of analysis, the data identities, the chart's preparation data and the species being quantitated.